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**A Study of the Adsorption of Acetonitrile on a Gold Electrode from Aqueous Solutions Using In
Situ Vibrational Spectroscopy**

by

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**A Study of the Adsorption of Acetonitrile on a Gold Electrode from Aqueous
Solutions Using In Situ Vibrational Spectroscopy***

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* Dedicated to Professor Ernest Yeager on the occasion of his retirement from Case Western Reserve University and in recognition of his contribution to electrochemistry.

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Abstract

The structure of the interphase at the gold/aqueous solution interface with adsorbed acetonitrile was studied by subtractively normalized FTIR spectroscopy (SNIFTIRS). Two types of acetonitrile and water molecules were observed in the interphasal region. The first involved chemisorbed molecules in which important vibrational modes are strongly shifted in frequency with respect to that observed in the bulk of the solution. In the case of acetonitrile, adsorption resulted in a $C \equiv N$ stretching band at 2342 cm^{-1} , and for water, a bending mode at 1688 cm^{-1} . The second type of molecule in the double layer with a band at 2261 cm^{-1} in the case of acetonitrile, and at 1628 cm^{-1} in the case of water was assumed to be hydrogen bonded to chemisorbed water molecules, and thus located further away from the geometrical interface. A band due to perchlorate ion at 1107 cm^{-1} is attributed to anions attracted into the double layer by the positive charge on the electrode. No evidence was obtained for contact adsorption of this anion.

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Introduction

Infrared reflectance spectroscopy has proven to be a powerful tool for investigating the structure of the electrode/solution interface [1-3]. Early work included studies of molecular and ionic adsorption, and investigations of species in the double layer [1,2]. In a study carried out in pure acetonitrile, Pons et al [4,5] showed that when acetonitrile is adsorbed on platinum, there is a strong shift in the $C \equiv N$ stretch frequency to higher wave numbers. This can be interpreted as evidence that the acetonitrile molecule is adsorbed through the nitrogen atom so that the non-bonding electrons interact strongly with the atoms of the metal. It is well known that bonding of acetonitrile to metal cations [6,7] also results in a blue shift in the $C \equiv N$ stretch frequency, but to a much smaller extent.

The purpose of the present experiments was to examine the adsorption of acetonitrile from aqueous solutions at a gold electrode. Gold behaves as a polarizable electrode over a wider potential range than platinum, and well established techniques have been developed to determine the extent of organic adsorption at both polycrystalline and single crystal electrodes [8,9]. By observing the characteristics of acetonitrile molecules adsorbed from aqueous solution, one has a means of distinguishing adsorbed molecules from those in the diffuse part of the double layer or in the bulk of the solution. In this way, one can gather the necessary information for interpreting vibrational reflection spectra obtained in pure acetonitrile. The electrolyte used in the experiments was $KClO_4$, it having been shown elsewhere that the K^+ cation has a very small effect on the spectrum of acetonitrile [7]. The spectroscopic technique used was subtractively normalized interfacial FTIR spectroscopy (SNIFTIRS) as developed by Pons and colleagues [1,2].

Experimental

Spectroelectrochemical Cell

The configuration of the electrodes mounted in a teflon holder is shown on Fig. 1a. The working electrode was a gold disc with a diameter of ~ 1 cm. It was surrounded by a concentric loop of gold wire with a diameter of ~ 3 cm, which served as counter electrode. A saturated calomel reference electrode was connected to the body of the cell by a hole drilled in the teflon holder between the working and counter electrodes. Other holes in the teflon holder provided a means of flushing the solution being investigated into and out of the small space between the gold working electrode and the ZnSe window. The cell arrangement shown provides a good throughput of infrared energy but results in high cell resistance and asymmetric current distribution. In the case of the present double layer studies, these drawbacks are not important. A side view of the cell showing the path of the infrared light with respect to the ZnSe window and gold electrode is shown in Fig. 1b. The light exiting the interferometer is reflected by a mirror, and then passes through the ZnSe window and a thin layer of solution to the gold electrode. On reflection at the gold it is sent back through the solution and window to the detector via a second reflecting mirror.

The Experiment

The spectra were obtained with a Bruker FTIR spectrometer (IFS 113 V) using a HgCdTe detector cooled with liquid nitrogen. The electrolyte solution, which was purged well with nitrogen, flowed through the cell continuously while spectroscopic data were collected. The spectra were recorded with the optical bench evacuated in the wavelength range from 1000 to 3000 cm^{-1} with a resolution of 8 cm^{-1} , and were obtained with no less than 500 scans at each potential. The gold electrode potential was controlled using the sample switching device described earlier [10], using two different cycling patterns as described below. This device consisted of a sample number decoder, a voltage range selector and a potentiostat. The decoder responds to commands from the Aspect 2000 computer built into the spectrometer and activates the potentiostat according to a pre-programmed scheme. Spectra Calc software (Galactic Industries) was used to subtract

spectra obtained at a given potential from that at the reference potential and to plot the resulting SNIFTIR spectra.

The Gold Electrode

The gold disc embedded in KelF holder was polished with successively finer grades of alumina powder down to 0.05 μm . It was thoroughly washed in an ultrasonic bath and with nanopure water. It was chemically treated in a series of solutions involving HF, NaOH, HNO_3 and H_2SO_4 in sequence as described earlier [11,12].

Chemicals

Acetonitrile (Aldrich, Gold Label) was used without further treatment. Potassium perchlorate (Fluka) was recrystallized from nanopure water and dried at 170 $^\circ\text{C}$ in an evacuated oven. Perchloric acid (Aldrich, 99.999%) was used as received. All solutions were made in nanopure water.

Results

Cyclic voltammograms obtained in the cell described above containing aqueous solutions of (a) 0.2 M HClO_4 and (b) 0.1 M CH_3CN and 0.05 M KClO_4 at a scan rate of 10 mV s^{-1} are shown in Fig. 2. The data obtained in the acid solution are similar to those reported earlier [13] and indicate that oxidation of the gold electrode commences at 1.08 V. The cyclic voltammogram recorded in the KClO_4 solution containing acetonitrile demonstrates that oxidation commences at a less positive potential. An anodic peak just positive of 1.0 V is barely visible and two cathodic peaks are found at potentials more negative than the single peak observed in the acidic solution. This behaviour is similar to that found by Iannelli et al. [14] when pyrazine is adsorbed on a polycrystalline gold electrode from aqueous solution. It is clear that the presence of acetonitrile affects the reduction of the gold oxide formed in the positive going sweep.

The SNIFTIRS data were obtained using two different potential step schemes, the first of which is illustrated in Fig. 3. The reference potential E_r was -0.80 V with respect to a SCE, that is, close to the potential at which deposition of hydrogen begins. The spectrum was recorded at the reference potential and then at a more positive potential, and the difference spectrum calculated. After each positive excursion the electrode potential was returned to the reference value for approximately 30 s. The electrode potential was then stepped to a potential more positive than the previous one by 150 mV and the process repeated. SNIFTIR spectra obtained in the $\text{C} \equiv \text{N}$ stretch region are shown in Fig. 4. Two potential dependent bands are observed at 2261 cm^{-1} and 2342 cm^{-1} . The higher frequency band is more intense and varies more with potential than the band at 2261 cm^{-1} . Keeping in mind that the $\text{C} \equiv \text{N}$ stretch in pure acetonitrile occurs at 2253 cm^{-1} [15], and that this band is strongly shifted in the blue direction when acetonitrile is adsorbed on platinum [4,5], it is reasonable to conclude that the band at 2342 cm^{-1} is due to acetonitrile adsorbed on the gold electrode. The band at 2261 cm^{-1} occurs at the same frequency as that for an acetonitrile molecule which is hydrogen bonded to a water molecule in the bulk of the solution [16]. Thus, this band in the interfacial spectrum is attributed to an acetonitrile molecule bonded through

the nitrogen atom to a water molecule which is itself adsorbed on the electrode. Further evidence relevant to this conclusion is presented below.

Spectra obtained in the region from 1450 to 1850 cm^{-1} are shown in Fig. 5a. The spectral features centered at 1660 cm^{-1} are attributed to water and suggest that this molecule is strongly chemisorbed to an extent which increases as the electrode potential is made more negative. It should be noted that the water bending mode is observed at 1600 cm^{-1} in the vapor phase so that the bands found in the differential interfacial spectra are blue shifted with respect to the vapor phase band. The broad band centered at 1660 cm^{-1} can be resolved into two bands with Lorentzian shapes with maxima at 1688 and 1628 cm^{-1} . As can be seen from Fig. 5b, the fitted spectrum on the basis of two Lorentzian bands provides an excellent description of the broad band centered at 1660 cm^{-1} . The origin of these two bands with respect to the molecular description of the interface is discussed in more detail below. Finally, the adsorption of perchlorate into the double layer is seen from the band at 1107 cm^{-1} which increases in intensity with excursion of the electrode potential in the negative direction. The simple nature of this band indicates that the perchlorate ion is not ion paired [15] and that it is not contact adsorbed at the electrode. The latter would require that it displaces either water or acetonitrile molecules which are themselves strongly chemisorbed at positive potentials. It would also result in a change in the vibrational features of perchlorate ion from those seen in the bulk of the solution.

The other potential modulation scheme involved driving the electrode to a far positive potential (+1.50 V) for a short period of time before bringing it back to the value at which the spectrum was recorded (see Fig. 6). As a result, an oxidation process occurs at the electrode, the products of this reaction be reduced or partially reduced before the spectrum is recorded. Otherwise, the potential-time program is similar to that described above. Difference spectra in the region from 1000 to 2500 cm^{-1} are shown as a function of electrode potential in Fig. 7. There are two positive going bands at 2342 and 1107 cm^{-1} , and two negative going bands at 2261 and 1689 cm^{-1} . The latter two bands occur at the same frequencies where positive going bands were observed in the experiments carried out using the first potential modulation scheme. In addition, there is a bipolar

band with its zero crossing at 1632 cm^{-1} and positive lobe at 1596 cm^{-1} . The bipolar band is probably associated with the band at 1628 cm^{-1} observed in the previous experiments.

Intensity data for the C-N stretching bands based on integrated band areas are presented in Fig. 8. The intensity of the band at 2342 cm^{-1} rises quickly as the potential is made more positive, reaches a plateau and then falls somewhat at the most positive potentials. The intensity against potential profile is somewhat different when the potential modulation scheme involving preliminary oxidation is used. In this case, the sharp rise in intensity occurs at a more positive potential and the maximum value on the plateau is somewhat less. For the bands at 2261 cm^{-1} , the intensity variation with potential is much less, a small increase being observed for the experiments carried out with the positive going pulse. On the other hand, when the electrode is pre-oxidized the intensity of the band at 2261 cm^{-1} slowly decreases as the electrode potential becomes more positive. The potential dependence of the water bands observed in the spectra obtained with the positive going pulse are shown in Fig. 9. The band at 1628 cm^{-1} is more intense than that at 1688 cm^{-1} , and both bands increase in intensity as the potential becomes more positive. The fact that the slope of the intensity against potential plot is decreasing suggests that the adsorption of water would approach a limiting value if it were not oxidized. Finally, intensity against electrode potential plots for the asymmetric stretch mode of the perchlorate anion is shown in Fig. 10. In this case, the data obtained from experiments using the two potential modulation schemes are the same within experimental error. As one would expect, adsorption of ClO_4^- on the electrode surface increases as the electrode potential becomes more negative.

Discussion

The spectra obtained in the present SNIFTIRS experiments show interesting features in the double layer region on gold. These features relate not only to the absorption of acetonitrile, but also to the adsorption of water and perchlorate ions. The significance of the spectral details with respect to the change in composition of the interfacial region at the gold electrode is now considered in more detail.

The band at 2342 cm^{-1}

Coordination of acetonitrile to a cation usually results in a shift in the $\text{C} \equiv \text{N}$ stretch frequency in the blue direction, the extent of which depends on the charge to radius ratio for the cation. The largest shift for a cation is observed for Mg^{2+} (36 cm^{-1}) [15], which also has the largest z/r ratio for the cations which have been studied [7]. The present shift of 89 cm^{-1} for acetonitrile adsorbed on gold is much larger, and comparable to that found for the adsorption of acetonitrile on platinum (98 cm^{-1}) [4]. It is also similar to the blue shift of 100 cm^{-1} observed when acetonitrile forms an adduct with BF_3 , a strong Lewis acid [17]. The fact that the $\text{C} \equiv \text{N}$ stretch frequency is shifted to higher values is attributed to the removal of electron density from antibonding orbitals so that the net bond order increases [18]. These observations provide strong evidence that the acetonitrile molecule is adsorbed so that the central axis of symmetry is perpendicular to the surface with the nitrogen atom coordinated to a metal atom of the electrode. On the basis of the harmonic oscillator model [16], it is estimated that the force constant of this bond increases by 7 percent on coordination with the gold surface. Comparing the present results with those for formation of an adduct with BF_3 , it is clear that the metal electrode behaves very much like an electron deficient entity. It is also interesting to compare the interaction of the $\text{C} \equiv \text{N}$ group and the metal electrode with that observed earlier for carbon monoxide adsorbed on platinum [18-20]. The frequency of the $\text{C} \equiv \text{O}$ stretch for the adsorbed molecule depends on electrode potential [18-20], whereas that for the $\text{C} \equiv \text{N}$ stretch in adsorbed acetonitrile does not. This is taken as evidence that donation of electron density from the non-bonding electrons on nitrogen dominates the adsorption process in the case of acetonitrile, and that back bonding from d orbitals of the metal to the π^* orbitals of the molecule does not play a role.

In the case of the adsorption of carbon monoxide, the latter process is assumed to be important [19-21]. As a result, the adsorption of acetonitrile on metal electrodes leads to a strengthening of the $C \equiv N$ bonds, whereas the adsorption of carbon monoxide results in a weakening of the $C \equiv O$ bond.

The band at 2261 cm^{-1}

This band occurs at the same frequency as that for the $C \equiv N$ stretch when acetonitrile is coordinated to water via hydrogen bonding [16], and therefore is assigned to a surface species involving these molecules. The band is positive going in the experiments involving the direct positive pulse, but negative going in the experiments in which the electrode is preoxidized. These results provide clear evidence that the signal originates with a surface species. It is interesting to speculate on the orientation of the adsorbed species with respect to the electrode. One possibility is that the two molecules interact while adsorbed with their dipole vectors parallel to the interface. This orientation would allow maximum interaction of the π electron density of the $C \equiv N$ bond with the electrode. However, in this case the frequency of the $C \equiv N$ stretch would shift strongly to lower frequencies (ca. 1700 cm^{-1}) [22]. Another possibility is that the acetonitrile molecule is adsorbed with the positive end of its dipole (CH_3 group) directed to the metal surface and the negative end interacting with a water molecule further away from the electrode in the double layer. However, in this orientation the acetonitrile dipole is in the orientation of high energy with respect to the electrode field so that it is difficult to accept that the coverage of the electrode by such a species increases as the electrode potential is made more positive (Fig. 4). The final possibility and that considered most probable involves interaction of acetonitrile in the double layer with an adsorbed water molecule. In this case, the orientation of both the water and acetonitrile dipoles are in the lowest energy configuration with respect to the electrode field when it is positive. Furthermore, the changes in the intensity of this band with potential follow those for the band at 1688 cm^{-1} which is attributed to chemisorbed water molecules. These interesting observations provide strong evidence that there are two mechanisms by which acetonitrile is adsorbed in the

double layer, namely, directly on the electrode through the nitrogen end of the molecule, and indirectly, by hydrogen bonding through the nitrogen atom with chemisorbed water.

The bands at 1688 and 1628 cm^{-1}

The water bending frequency, ν_2 , is reported to be 1595 cm^{-1} in the gas phase [23], 1640 cm^{-1} in liquid water [24] and 1620 cm^{-1} in ice [25]. It is clear that hydrogen bonding present in the liquid and solid phases results in a blue shift from 25 to 45 cm^{-1} . It is reasonable to expect that interaction of the oxygen end of the water dipole with the atoms of the metal electrode results in an even larger increase in the ν_2 frequency so that the band at 1688 cm^{-1} is assigned to the ν_2 mode in the chemisorbed water. It also follows that the band at 1628 cm^{-1} is due to water molecules which are further away in the double layer and hydrogen bonded to the chemisorbed molecules on the surface. Although these assignments are based solely on band frequencies, they are supported by other observations. Firstly, the intensity of the bands is potential dependent, becoming stronger as the electrode potential is made more positive in a direct positive going potential jump. This suggests that the chemisorption of water on the gold electrode increases with the same potential change. This conclusion is completely compatible with impedance data obtained under the same conditions [11] and would be an understandable precursor to electrode oxidation. The second observation relevant to the present interpretation is the fact that these bands appear differently when the different potential modulation schemes are used. Especially important is the appearance of the bipolar band in the experiments in which the electrode is preoxidized. When the electrode is oxidized, the chemisorbed water is undoubtedly converted to oxide with a resulting drop in pH near the electrode [26]. This step is also accompanied by surface reconstruction [26]. The fact that there is a negative going band at 1688 cm^{-1} in these experiments suggests that the surface concentration of chemisorbed water is less on the preoxidized electrode surface than at the negative reference potential. This observation is attributed to the fact that all of the oxide on the surface has not been reduced back to the metal and water molecules. It is also partially due to the fact that the experiments are carried out under flow conditions so that the protons produced on oxidation are flushed away from the electrode before reduction takes place. Under these circumstances,

hydroxyl ions would be produced near the electrode. Since the small volume between the electrode and window may not be efficiently exchanged during the time of the oxidizing pulse, that latter process probably does not contribute significantly to the magnitude of the negative going band. Because of the complex nature of the spectra in this region for the preoxidized electrode, further analysis is not possible.

It should also be noted that acetonitrile molecules adsorbed with their dipole vectors parallel to the electrode surface should have a $C \equiv N$ stretching vibration in this region. However, according to surface selection rules, this band should be weak in the infrared. If weak absorption occurs, it is masked by the water bands discussed above.

The band at 1107 cm^{-1}

Perchlorate anion has an asymmetric stretching mode, ν_3 , which is observed in solution at 1107 cm^{-1} [7]. If the anion is adsorbed on the electrode, its symmetry is reduced, and splitting of the band at 1107 cm^{-1} would occur. The fact that a well defined single band is observed in the spectra obtained suggests that perchlorate is not adsorbed on the electrode, but instead remains in the diffuse layer. As the electrode potential is made more positive, the electrode field attracts anions into the double layer and repels cations. As a result the surface signal for perchlorate increases. No other bands due to splitting of the band at 1107 cm^{-1} were observed. Thus, it is concluded that ClO_4^- anion does not specifically adsorb on gold for the present experimental conditions. These conclusions do not eliminate the possibility that the anion is adsorbed via hydrogen bonding to chemisorbed water molecules as is the case for some acetonitrile molecules in the double layer. Thus, our observations do not exclude the presence of perchlorate anions in the double layer for other than electrostatic reasons.

The Model of the Double Layer

The spectra obtained in the present study allow one to develop a more detailed model for the interfacial region at the gold electrode. Such a model is shown schematically in Fig. 11. The important result of the present experiments is that there are two types of acetonitrile adsorbed in the interphase. The first involves molecules which interact directly with the surface. Only one

orientation is observed, namely, that for molecules with their dipole vectors perpendicular to the interface and the negative end on the surface. The second type involves acetonitrile molecules hydrogen bonded to chemisorbed water molecules. The same conclusion is reached regarding water in the double layer. The chemisorbed layer absorbs at 1688 cm^{-1} and a second layer present through hydrogen bonding with the first absorbs at 1628 cm^{-1} . It should be noted that the dipoles chemisorbed and present further away from the interface due to hydrogen bonding can all be present in the orientation of lowest energy when the electrode field is positive. Finally, there is no evidence for contact adsorption of perchlorate in the present results. However, perchlorate is clearly attracted into the double layer for electrostatic reasons. Some of the surface excess of this anion may result from hydrogen bonding with chemisorbed water molecules.

The above details clearly provide more information about the adsorption of acetonitrile than would be available on the basis of thermodynamic data alone. They also provide the basis for studying the adsorption of cations in the double layer from solutions of pure acetonitrile in the study of underpotential deposition. In such a system, one should be able to distinguish three types of acetonitrile molecules in a SNIFTIRS study, namely those adsorbed on the electrode, those associated with metal cations, and those whose $\text{C} \equiv \text{N}$ stretching frequencies are essentially the same as the unperturbed molecule in the bulk of the solution. Experimental results dealing with such a study will be presented in a future paper.

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Legends for Figures

- Figure 1.** Schematic diagram of the electrochemical cell (a) from the top, and (b) from the side.
- Figure 2.** Cyclic voltammograms obtained at a gold electrode with a scan rate of 10 mV s^{-1} with (a) an aqueous solution containing 0.20 M HClO_4 , and (b) an aqueous solution containing 0.05 M KClO_4 and $0.10 \text{ M acetonitrile}$.
- Figure 3.** Potential against time plot for the modulation scheme in which the electrode potential is stepped from the reference potential (-0.80 V) to a more positive potential at which the FTIR spectrum is recorded. The potential step increases by $+150 \text{ mV}$ in successive excursions as illustrated.
- Figure 4.** SNIFTIR spectra obtained in the $\text{C} \equiv \text{N}$ stretching region as a function of electrode potential. The spectra have been shifted vertically for clarity.
- Figure 5.** SNIFTIR spectra obtained in (a) the 1850 to 1450 cm^{-1} , and (c) 1350 to 950 cm^{-1} regions as a function of electrode potential. The spectra have been shifted vertically for clarity. The spectrum obtained at 1.00 V in the 1850 to 1450 cm^{-1} region has been fitted in (b) to two Lorentzian bands at 1688 and 1628 cm^{-1} and the resulting residual shown.
- Figure 6.** Potential against time plot for the modulation scheme in which the electrode potential is stepped first to $+1.5 \text{ V}$ for and then quickly back to a less positive potential where the FTIR spectrum is recorded. The final potential step increases by $+150 \text{ mV}$ in successive excursions as indicated.
- Figure 7.** SNIFTIR spectra obtained in the 2500 to 1000 cm^{-1} region as a function of electrode potential using the potential modulation scheme in which the electrode is preoxidized. The spectra have been shifted vertically for clarity.
- Figure 8.** Dependence of the intensity change for the $\text{C} \equiv \text{N}$ stretching bands on electrode potential. The solid symbols refer to the bands at 2342 cm^{-1} and the open symbols to those at 2261 cm^{-1} . The circles refer to data obtained in the simple modulation

experiment and the triangles to data obtained in the modulation scheme in which the electrode is preoxidized.

Figure 9. Dependence of the intensity change for the water bending bands on electrode potential at 1688 cm^{-1} (o) and 1628 cm^{-1} (●). The data were obtained in the experiment with the direct positive going pulse.

Figure 10. Dependence of the intensity change for the perchlorate band at 1107 cm^{-1} on electrode potential. The data (o) were obtained in the experiment in which the electrode was preoxidized and the data (●) in the experiment without preoxidation.

Figure 11. Schematic diagram of the double layer indicating the location and orientation of chemisorbed acetonitrile and water, and the presence of ClO_4^- , acetonitrile and water further from the electrode in the diffuse layer.

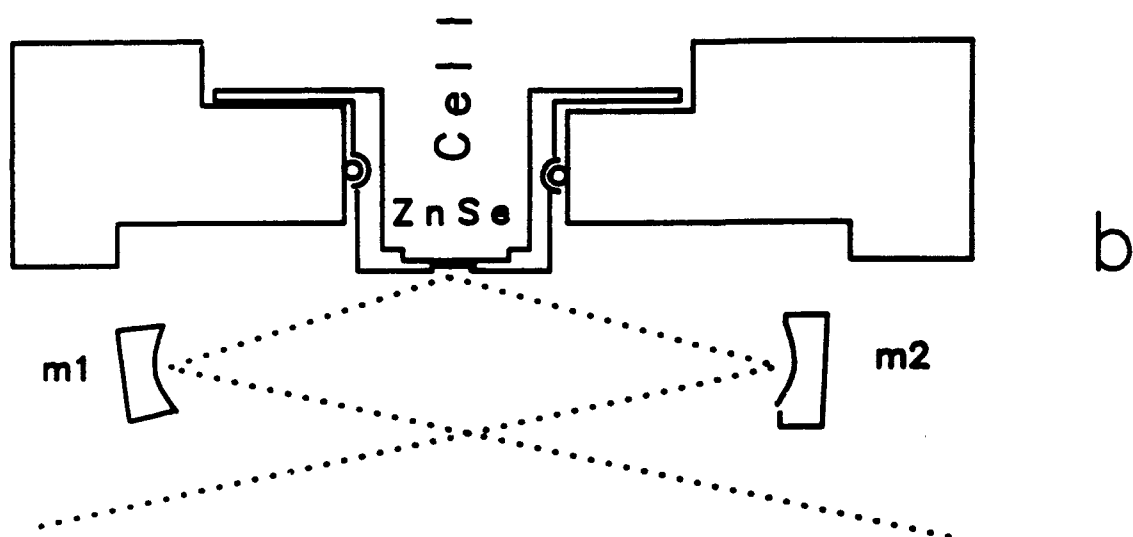
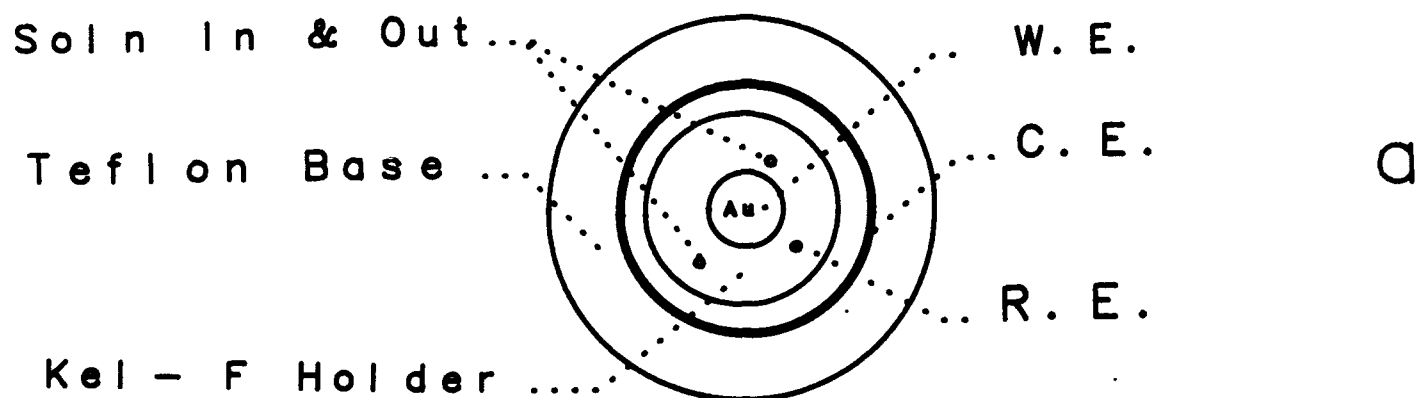
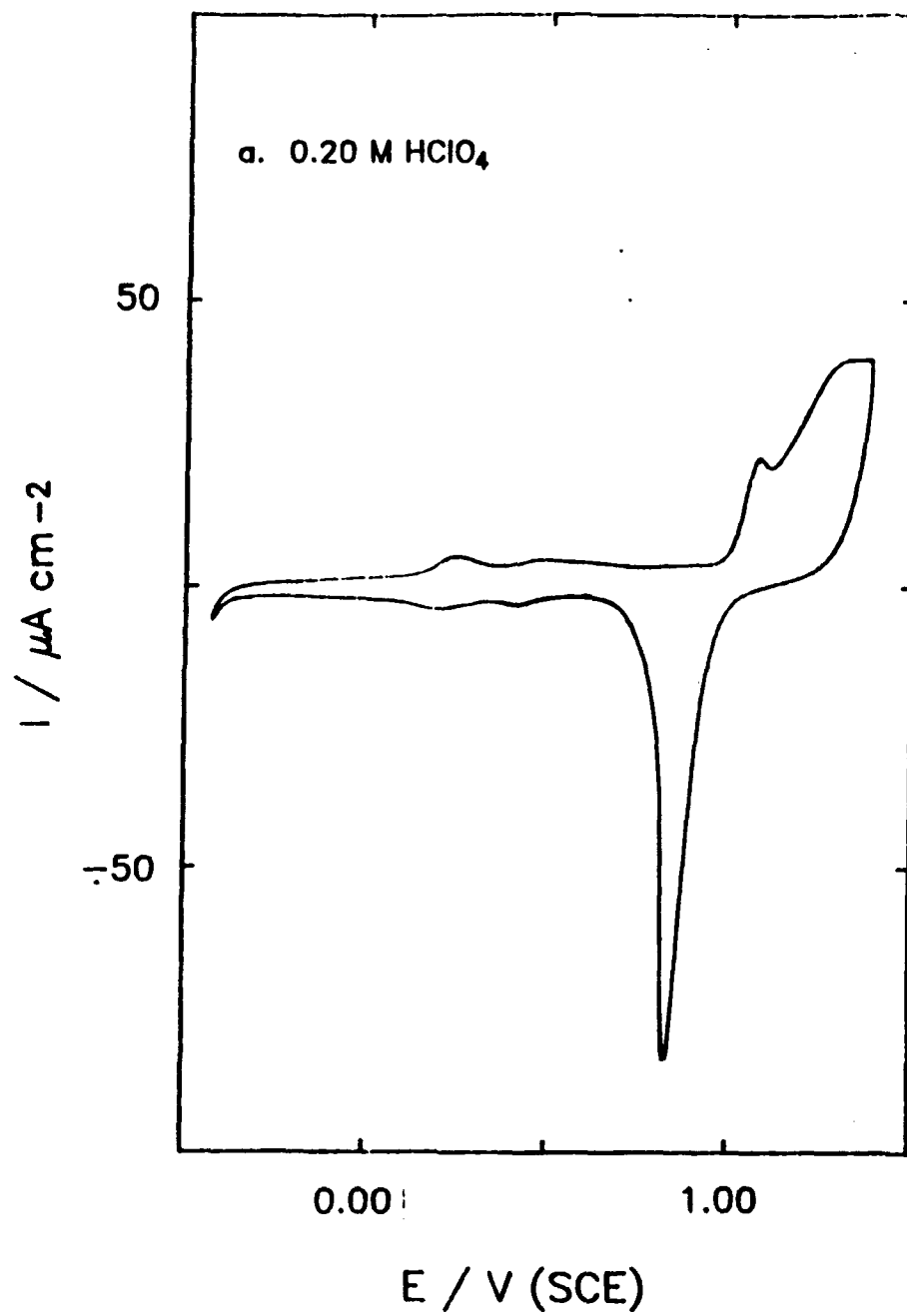


Fig 1. Faquy et al.



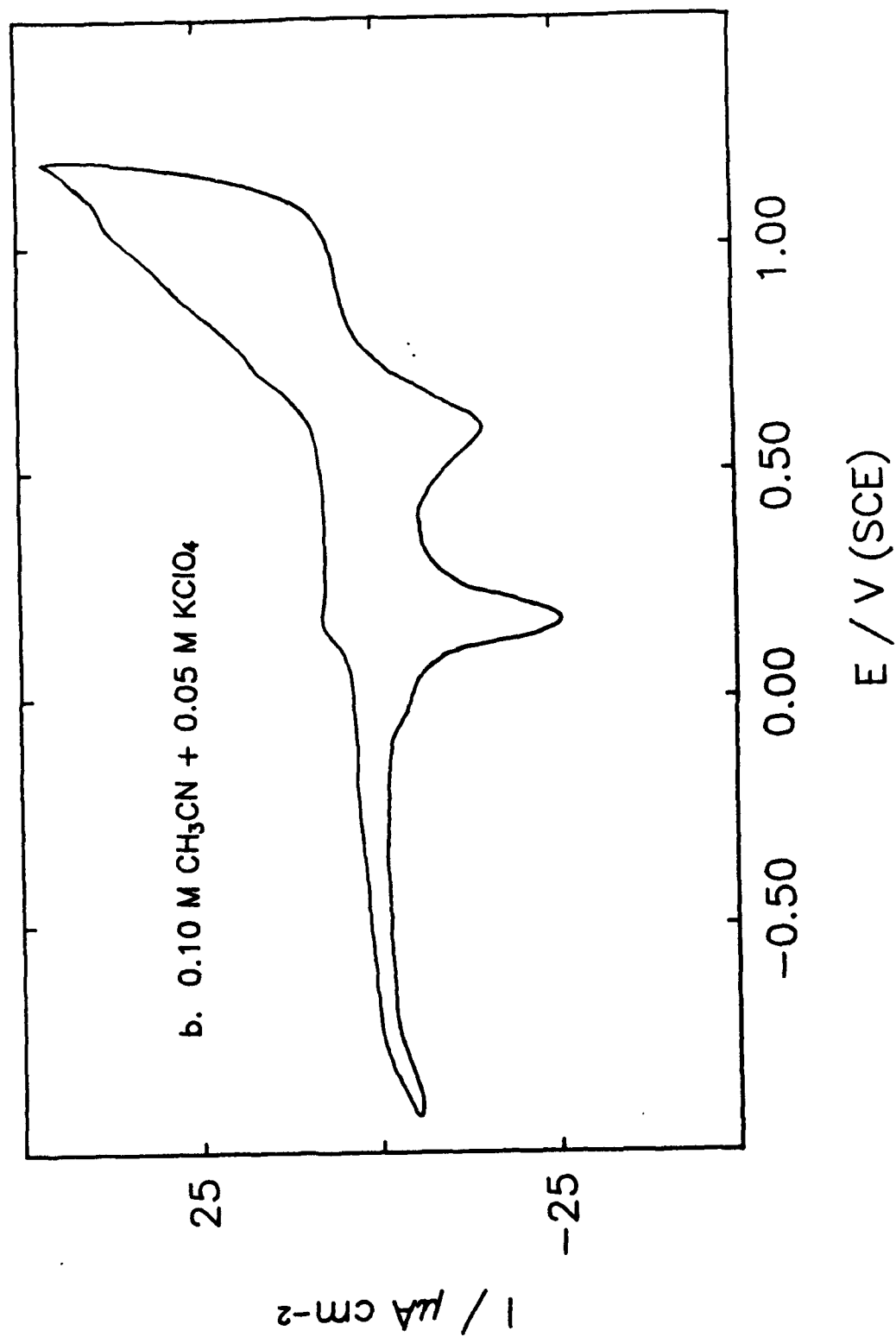
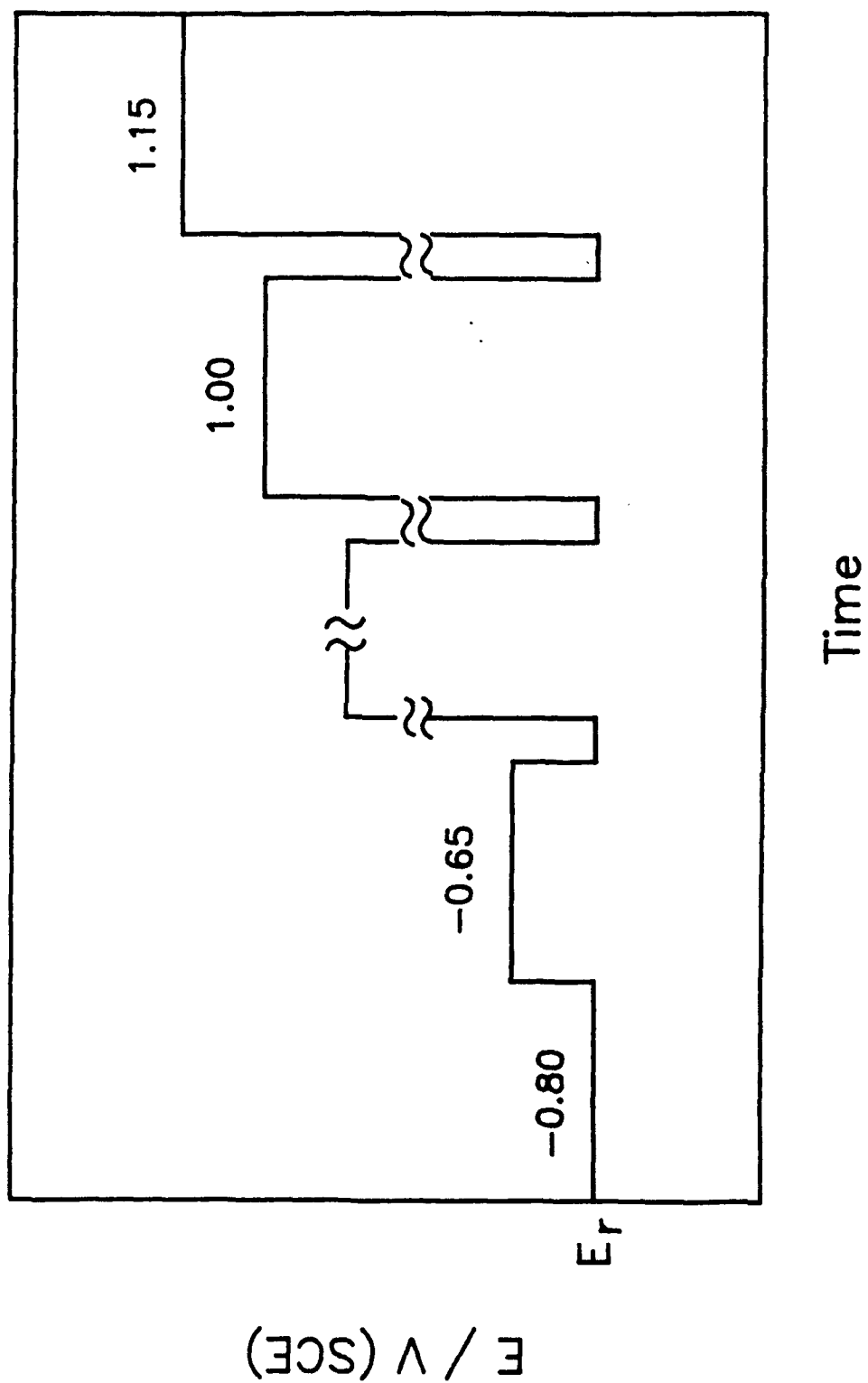
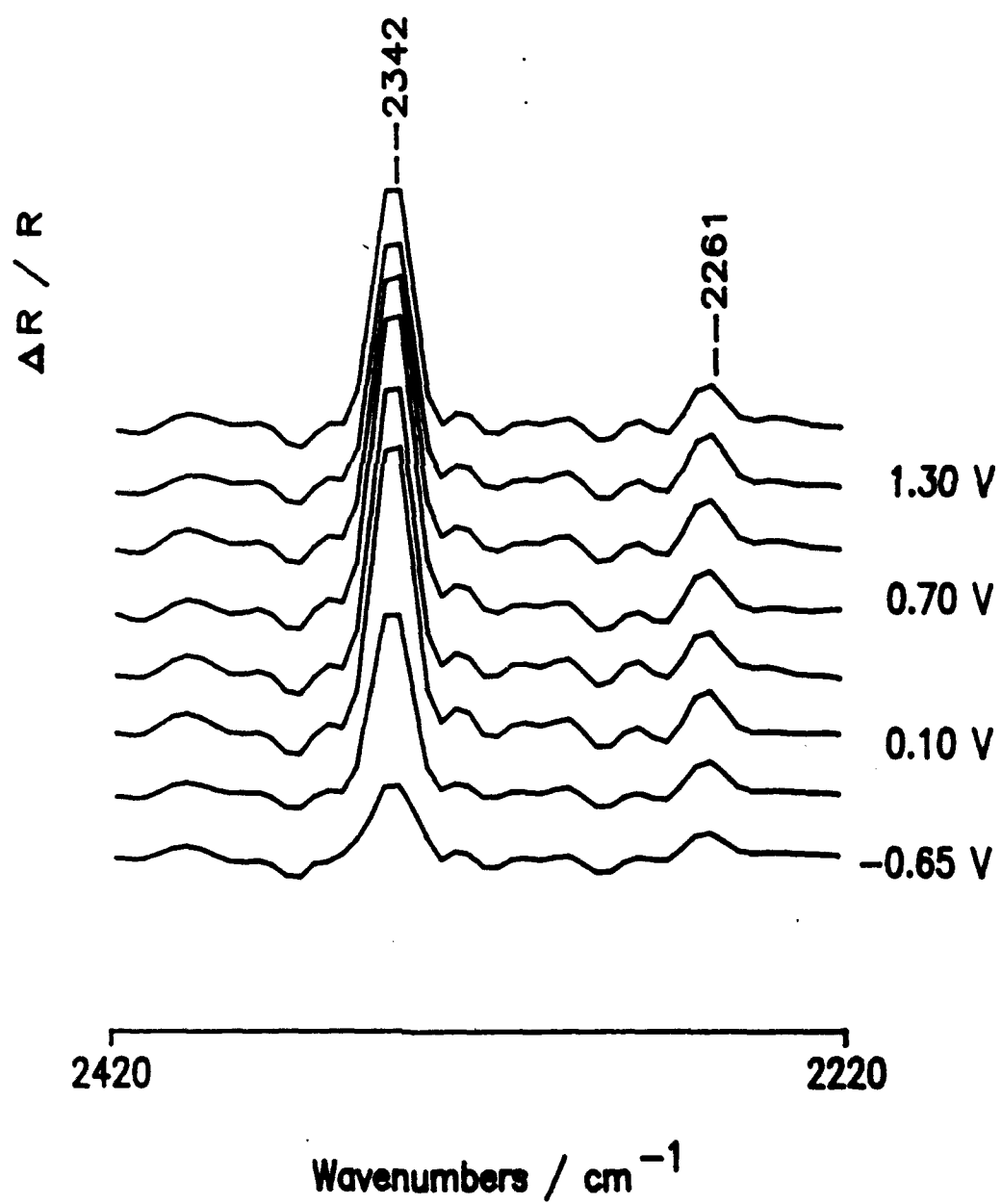
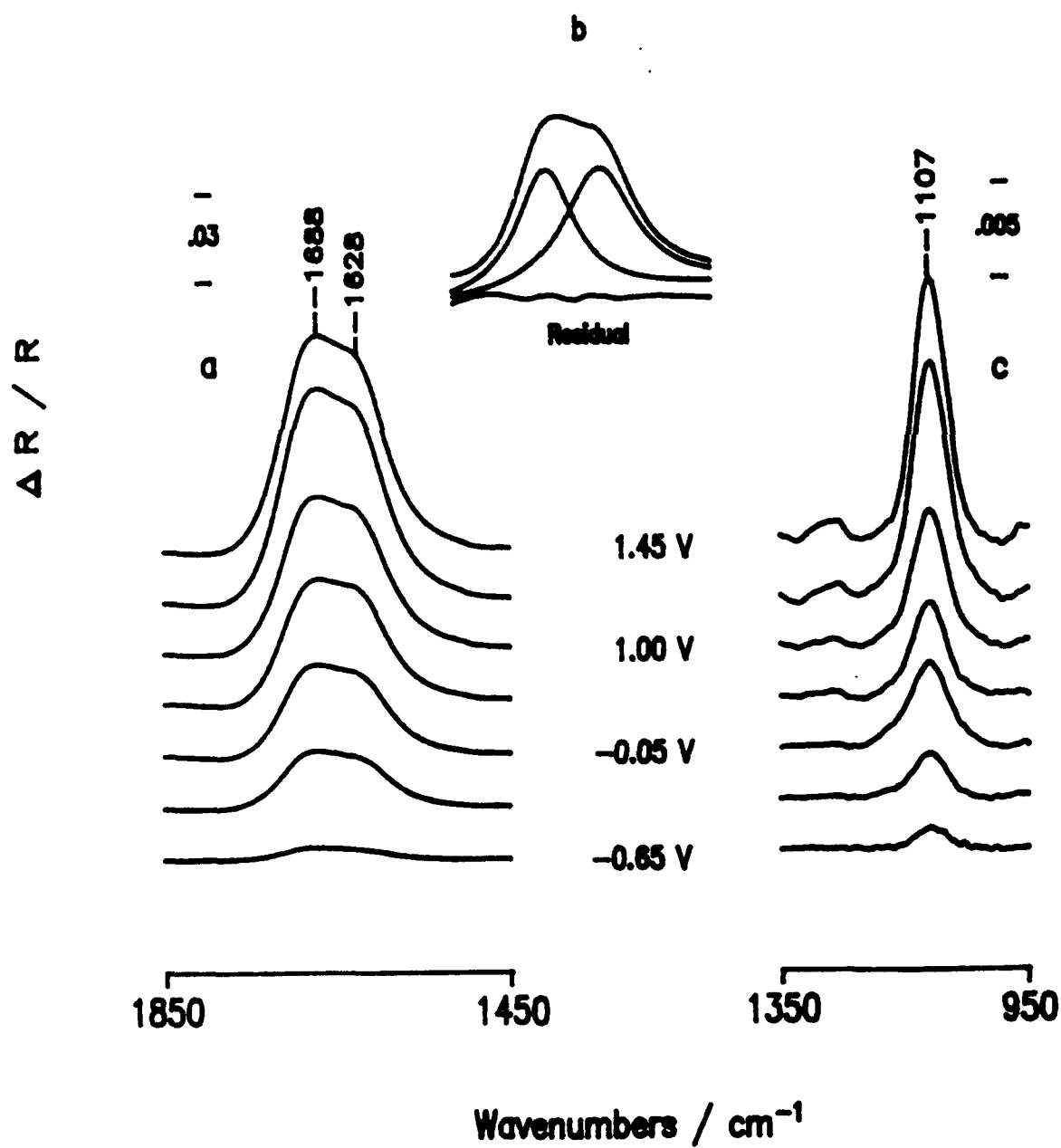


Fig.2b, Faguy et al.







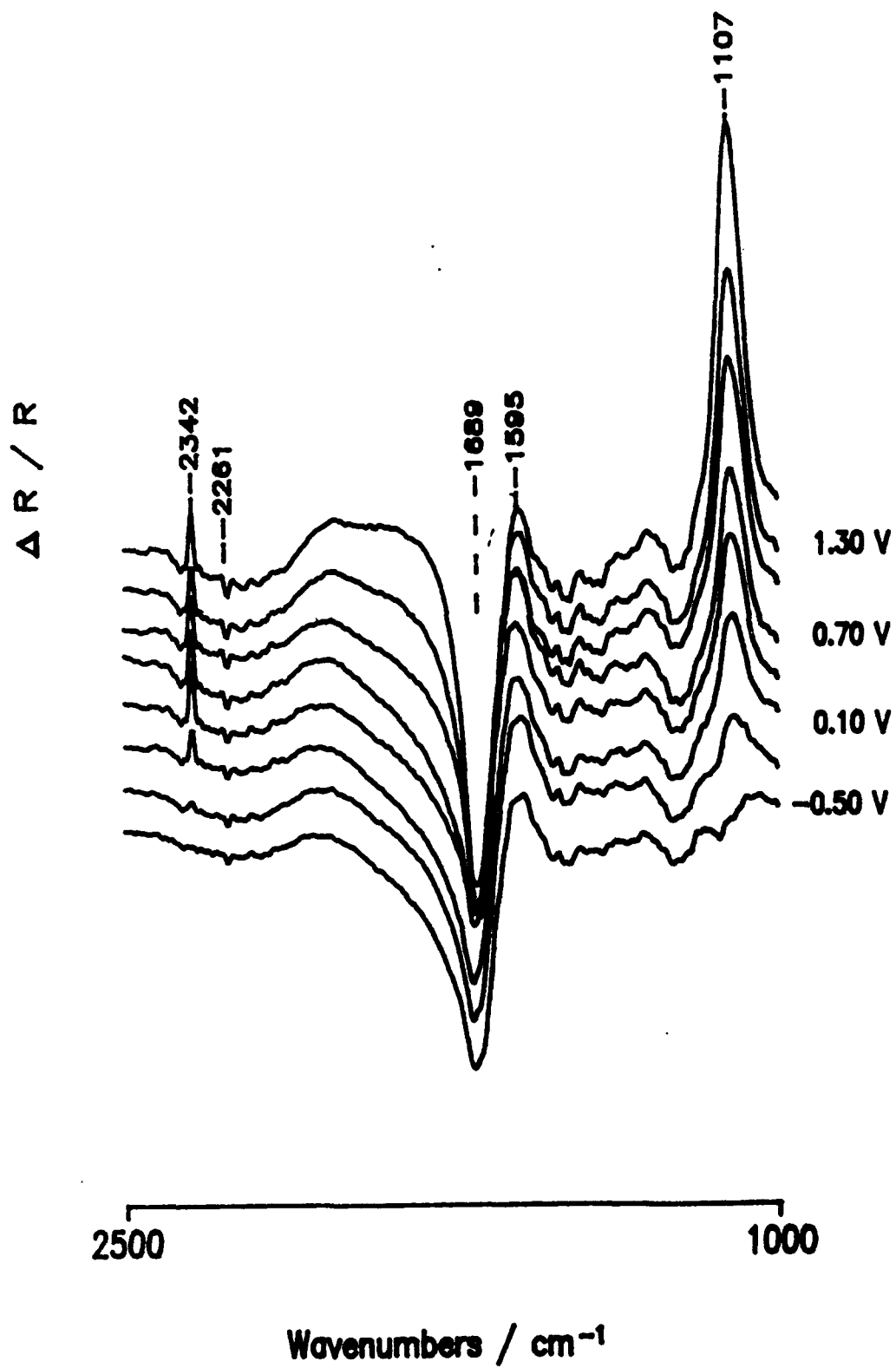


Fig.7. Faquy et al.

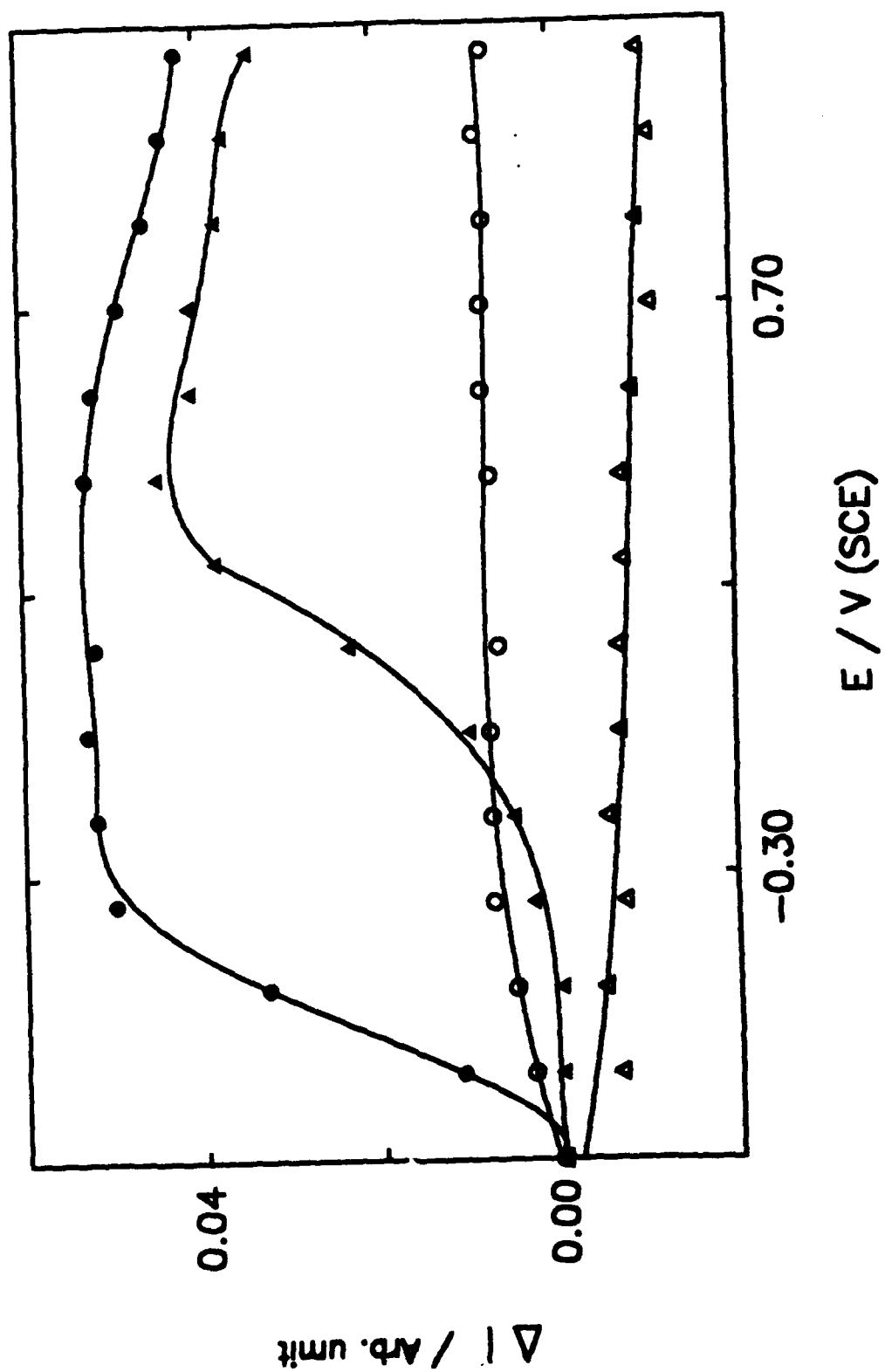


Fig. 2. Experimental

